

U.S. Patent Application Serial No. 10/588,796  
Response filed June 23, 2009  
Reply to OA dated February 24, 2009

### **REMARKS**

Claims 4 and 5 are pending in this application. Claims 4 and 5 are amended, and claims 6 and 7 are newly added herein. Upon entry of this amendment, claims 4-7 will be pending. Entry of this amendment and reconsideration of the rejections are respectfully requested.

No new matter has been introduced by this Amendment. Support for the amendments to the claims 4 and 5 is detailed below.

**Claims 4 and 5 are rejected under 35 U.S.C. §112, first paragraph, as failing to comply with the written description requirement. (Office action p. 2)**

The Examiner states that there is no written disclosure support for the limitation "which does not contain any inorganic acid salt of melamine."

The rejection is overcome by the amendments to the claims, in which this phrase is deleted.

**Claims 4 and 5 are rejected under 35 U.S.C. §112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention. (Office action p. 3)**

a) The Examiner states that "it is unclear whether the bisphenol-type epoxy resin or novolac-type epoxy resin is intended to further identify the epoxy-containing unsaturated compound (b); or

if it is added as a separate component, such as (C)." The Examiner states that he is interpreting the claims in view of Production Example 3.

The rejection is overcome by the amendments to claims 4 and 5. The amendments to claims 4 and 5 clarify the bisphenol-type epoxy resin or novolac-type epoxy resin is a separate component, and for clarity, it has been designated as "(C)" in the amendment. Support for the amendments to claims 4 and 5 is found on page 4, lines 8 to 16, and Examples 1 to 4 of the Specification.

b) The Examiner states that the terms "biphenol-type" and "novolac-type" are not defined.

Applicant notes that the term "biphenol" was a typographical error for "bisphenol," and this error has been corrected in the present amendment.

Applicant submits that the meanings of "bisphenol-type epoxy resin" and "novolac-type epoxy resin" are well known among those skilled in the art, as disclosed in Lee and Neville, "Handbook of Epoxy Resins" McGraw-Hill (1967), on page 2-2 to page 2-15. This document is attached to the present Response.

Specifically, the document discloses glycidyl ethers of bisphenol A as typical examples of epoxy resins on page 2-2 to page 2-10, sixth paragraph, and glycidyl ethers of other aromatic compounds from the third paragraph of page 2-12. Here, the glycidyl ethers of other aromatic compounds are synthesized by reacting an aromatic compound with epichlorohydrin (see page 2-12, third paragraph).

As one of other aromatic compound glycidyl ethers, glycidyl ethers of bisphenols are disclosed on page 2-12, sixth paragraph to page 2-15, first paragraph. Here, the definition of glycidyl ethers of bisphenols is the same as that of the bisphenol-type epoxy resin.

As is clear from the above, the bisphenol-type epoxy resin is an epoxy resin synthesized by reacting bisphenol with epichlorohydrin.

The document further discloses glycidyl ethers of novolac resins on page 2-10, seventh paragraph to page 2-12, second paragraph. The Figure on page 2-11 shows a specific glycidyl ethers of the novolac resins is the same as that of the novolac-type epoxy resin.

**Claims 4 and 5 are rejected under 35 U.S.C. §102(b) as being anticipated by Takao and Minoru (JP 2003-149475). (Office action p. 4)**

Reconsideration of the rejection of claims 4 and 5 is respectfully requested in view of the amendments to claims 4 and 5.

The Examiner cites paragraph [0006] of the reference as disclosing a mixture of an ethylenically unsaturated carboxylic resin (A), a diluent (solvent) (B), and a photopolymerization initiator (C). The Examiner cites paragraphs [0007]-[0008] as disclosing that carboxylic resin (A) is made of an epoxy resin (a), acrylic acid (b) and an optional component which has at least two epoxy groups, and which may be a bisphenol A-type resin bisphenol F-type resin or novolac resin. These components are considered to meet the limitations of components (a) and (b) in claims 4 and

5, and therefore of component (A). The Examiner states that "Production Example 3, disclosed as a preferred embodiment, is identical to Example 1 as disclosed by Takao and Minoru."

Takao and Minoru is a patent publication disclosing a resin composition for optical waveguides comprising: (A) an ethylenic unsaturated group-containing carboxylic resin that contains at least one ethylenic unsaturated group and at least one carboxyl group in the molecule, (B) a diluent, and (C) a photopolymerization initiator; and a curable composition thereof (see claims 1 and 3 of Takao and Minoru).

Applicant respectfully submits, however, that the machine English translation of paragraph [0007] of Takao and Minoru made by JPO is not correct, and should read as follows:

[0007] In this invention, an ethylenic unsaturated group-containing carboxylic resin (A) is used. Any ethylenic unsaturated group-containing carboxylic resin (A) can be preferably used, as long as the resin has at least one ethylenic unsaturated group and at least one carboxyl group in the molecule. Particularly preferable examples of the resin include a reactant obtained by the reaction between reactant (I) and a polybasic acid anhydride (d), wherein the reactant (I) is obtained by the reaction of (a) an epoxy resin having at least two epoxy groups in the molecule with (b) (meta)acrylic acid, and as an optional component, (c) a compound having one carboxylic acid and two hydroxyl groups in the molecule.

Accordingly, the ethylenic unsaturated group-containing carboxylic resin (A) disclosed in paragraph [0007] of Takao and Minoru is a reactant obtained by reacting the compound (d) with the reactant (I) of the following compounds (a) to (c):

Compound (a): an epoxy resin containing at least two epoxy groups in the molecule.

Compound (b): a (meta)acrylic acid.

Compound (c): a compound containing one carboxylic acid and two hydroxyl groups optional component).

Compound (d): a polybasic acid anhydride.

(1) In the present invention, a carboxy-containing unsaturated acrylic resin (A) has a carboxy-containing acrylic resin (a) backbone. The carboxy-containing unsaturated acrylic resin (A) is obtainable by reacting a carboxyl group in the carboxy-containing acrylic resin (a), with an epoxy group in the epoxy-containing unsaturated compound (b).

In contrast, the ethylenic unsaturated group-containing carboxylic acid (A) described in Takao and Minoru has an epoxy resin (a) backbone, as mentioned above. Epoxy groups in the epoxy resin (a) are first reacted with (meta)acrylic acid (b) and optionally with the carboxylic group of the compound (c), and then reacted with the compound (d) to form the ethylene unsaturated group-containing carboxylic acid (A).

Accordingly, the structure of the carboxy-containing unsaturated acrylic resin (A), which is recited in claims 4 and 5, is completely different from that of the ethylenic unsaturated group-containing carboxylic resin (A) disclosed in Takao and Minoru.

(2) As recited in amended claims 4 and 5, in the present invention, the carboxy-containing acrylic resin (a) can be obtained by reacting an  $\alpha,\beta$ -ethylenically unsaturated acid (selected from the group consisting of acrylic acid and methacrylic acid) with styrene in addition to at least one unsaturated monomer (selected from the group consisting of (meth)acrylates, (meth)acrylonitrile, and (meth)acrylamide).

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However, Takao and Minoru nowhere teaches styrene.

Therefore, claims 4 and 5, as amended, are not anticipated by Takao and Minoru (JP 2003-149475).

**Claims 4 and 5 are rejected under 35 U.S.C. §103(a) as being unpatentable over Takao and Minoru (JP 2003-149475) as evidenced by Sato et al. (U.S. Publication No. 2001/0003759).**  
(Office action p. 5)

Reconsideration of the rejection is respectfully requested in view of the amendments to claims 4 and 5.

As essential constituent elements, the present invention includes the following:

(A) a carboxy-containing unsaturated acrylic resin obtained by reacting a carboxy-containing acrylic resin (a) with an epoxy-containing unsaturated compound (b), the carboxy-containing acrylic resin (a) being obtained by copolymerizing at least one  $\alpha,\beta$ -ethylenically unsaturated acid selected from the group consisting of acrylic acid and methacrylic acid with styrene and at least one unsaturated monomer selected from (meth)acrylates, (meth)acrylonitrile, and (meth)acrylamide;

(B) a solvent; and

(C) a bisphenol-type epoxy resin or a novolac-type epoxy resin.

However, the compositions disclosed in "Takao and Minoru" and Sato et al. comprise an epoxy resin as a main component. Applicant submits first of all that there is no clear suggestion in the cited art for a specific carboxy-containing unsaturated acrylic resin (A) as an essential element.

As explained above, claims 4 and 5 as amended require combining styrene as a component of the carboxy-containing unsaturated acrylic resin (A) with an  $\alpha,\beta$ -ethylenically unsaturated acid and at least one unsaturated monomer. Neither the Takao and Minoru reference nor Sato et al. discloses styrene, and this limitation of the present claims is not suggested by the cited art.

Moreover, Applicant submits that there are **unexpected results** commensurate in scope with the present claims. Accordingly to the present invention, significant effects including high core shape precision can be obtained by using styrene as a reaction material of a carboxy-containing acrylic resin (a), the carboxy-containing acrylic resin (a) being reacted with an epoxy-containing unsaturated compound (b) to obtain a carboxy-containing unsaturated acrylic resin (A). To demonstrate this, Applicant here provides data in the attached Declaration under 37 CFR 1.132.

As stated above, an essential feature of the present invention lies in combining styrene as a material of the carboxy-containing unsaturated acrylic resin (A) with an  $\alpha,\beta$ -ethylenically unsaturated acid and at least one unsaturated monomer. Based on this feature, the present invention achieves significant effects, including high core shape precision. The data in the attached Declaration under 37 CFR 1.132 demonstrate the effect of high core shape precision.

Specifically, the Declaration provides a comparison of four waveguides (1) to (4) (see Table 1 on page 9), made respectively from four photocurable resin compositions (1) to (4) (see pages 2-4), which are used to make photocurable dry films (D-1) to (D-4) (pages 4-5). Compositions (1) and (2) are made using methyl methacrylate, styrene, butyl acrylate and acrylic acid, as well as glycidyl methacrylate. Compositions (3) and (4) are made using methyl methacrylate, butyl acrylate and

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acrylic acid, as well as glycidyl methacrylate. That is, compositions (3) and (4) are not made using styrene, and do not meet the limitations of the present claims. As can be seen in Table 1 on page 9, only waveguides (1) and (2) had a core that is not deformed by the upper cladding layer. This is an **unexpected effect** of the present invention.

Accordingly, claims 4 and 5 are not obvious over Takao and Minoru (JP 2003-149475) and Sato et al. (U.S. Publication No. 2001/0003759), taken separately or in combination.

#### **Regarding new claims 6 and 7**

Support for new claims 6 and 7 may be found in Production Examples 3 and 6. Since claims 6 and 7 are dependent from claims 4 and 5, respectively, the above arguments regarding the rejections of claims 4 and 5 are applicable to claims 6 and 7.

If, for any reason, it is felt that this application is not now in condition for allowance, the Examiner is requested to contact the applicants' undersigned agent at the telephone number indicated below to arrange for an interview to expedite the disposition of this case.

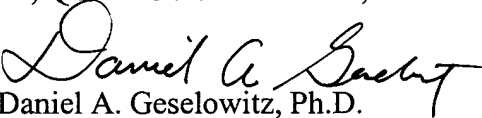


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In the event that this paper is not timely filed, the applicants respectfully petition for an appropriate extension of time. Please charge any fees for such an extension of time and any other fees which may be due with respect to this paper, to Deposit Account No. 01-2340.

Respectfully submitted,

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PATENT & TRADEMARK OFFICE

Enclosures: Petition for Extension of Time  
Lee and Neville, "Handbook of Epoxy Resins," pp. 2-2 to 2-15  
Declaration under 37 CFR 1.132 signed by Mr. Genji Imai

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## OTHER MCGRAW-HILL HANDBOOKS OF INTEREST

BEEMAN · Industrial Power Systems Handbook  
 BELL · Petroleum Transportation Handbook  
 BLATZ · Radiation Hygiene Handbook  
 CARROLL · Industrial Instrument Servicing Handbook  
 COCKRELL · Industrial Electronics Handbook  
 CONSIDINE · Process Instruments and Controls Handbook  
 CROCKER · Piping Handbook  
 ETHERINGTON · Nuclear Engineering Handbook  
 FACTORY MUTUAL ENGINEERING DIVISION · Handbook of Industrial Loss Prevention  
 FRICK · Petroleum Production Handbook  
 GRANT · Hackh's Chemical Dictionary  
 GUTHRIE · Petroleum Products Handbook  
 HEYEL · The Foreman's Handbook  
 HUSKEY AND KORN · Computer Handbook  
 JURAN · Quality Control Handbook  
 KALLEN · Handbook of Instrumentation and Controls  
 KATZ · Handbook of Natural Gas Engineering  
 KING AND BRATER · Handbook of Hydraulics  
 KNOWLTON · Standard Handbook for Electrical Engineers  
 KORN AND KORN · Mathematical Handbook for Scientists and Engineers  
 LANGE · Handbook of Chemistry  
 LASSER · Business Management Handbook  
 MAGILL, HOLDEN, AND ACKLEY · Air Pollution Handbook  
 MANAS · National Plumbing Code Handbook  
 MANTELL · Engineering Materials Handbook  
 MARKS AND BAUMEISTER · Mechanical Engineers' Handbook  
 MAYNARD · Industrial Engineering Handbook  
 MAYNARD · Top Management Handbook  
 MEITES · Handbook of Analytical Chemistry  
 MOODY · Petroleum Exploration Handbook  
 MORROW · Maintenance Engineering Handbook  
 PERRY · Chemical Engineers' Handbook  
 PERRY · Engineering Manual  
 RICHEY, HALL, AND JACOBSEN · Agricultural Engineers Handbook  
 SHAND · Glass Engineering Handbook  
 STANJAR · Plant Engineering Handbook  
 STREETER · Handbook of Fluid Dynamics  
 TOULOUKIAN · Retrieval Guide to Thermophysical Properties Research Literature  
 TRUXAL · Control Engineers' Handbook

# HANDBOOK OF EPOXY RESINS

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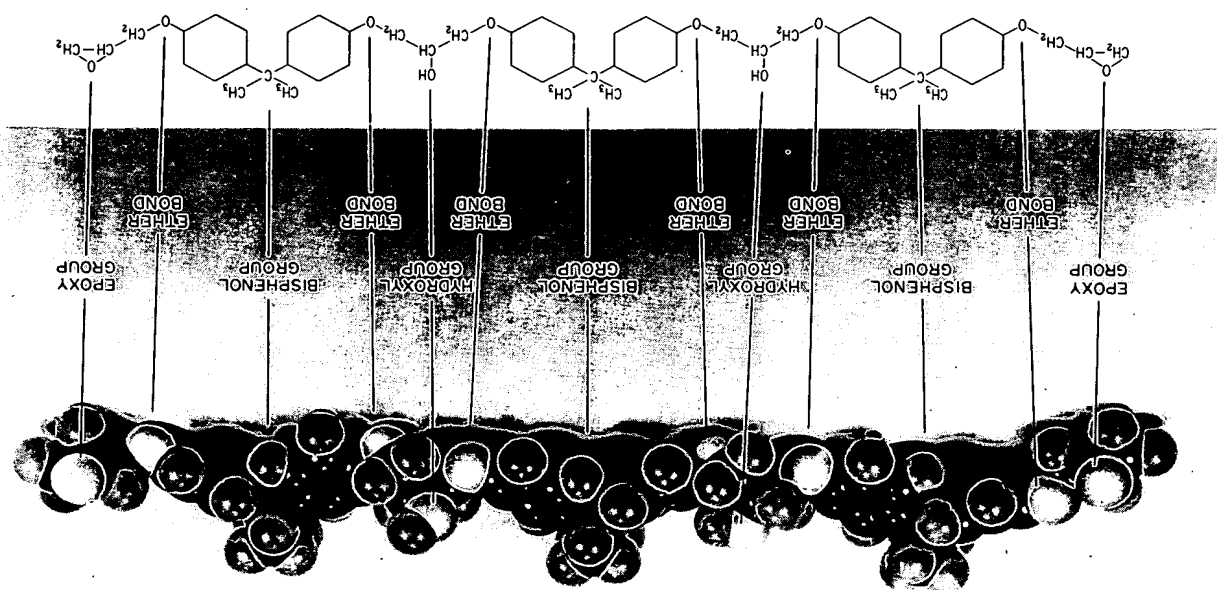


# HANDBOOK OF EPOXY RESINS

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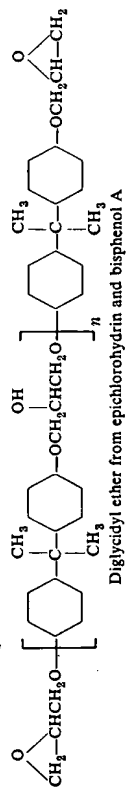
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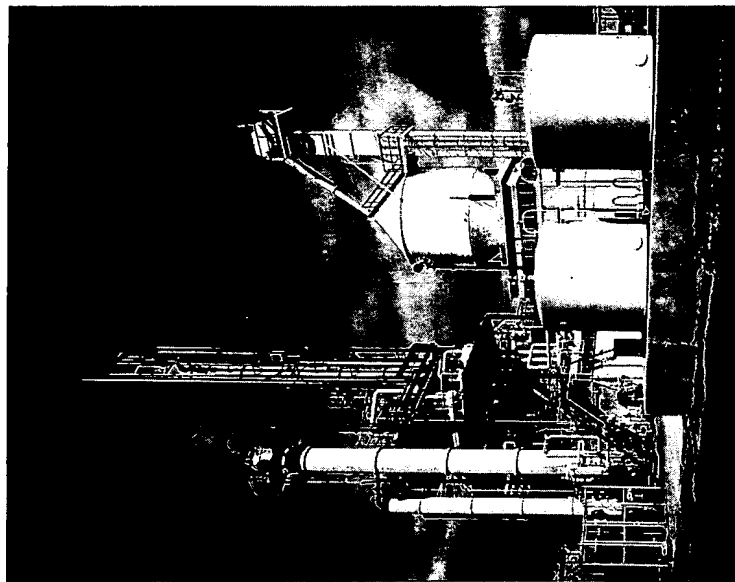
Atom model of widely used solid epoxy resin, diglycidyl ether of bisphenol A, degree of polymerization of 2 (DGEBA,  $n = 2$ ). Approximate magnification: 100 million times. (*The Epoxylite Corporation*.)

The first commercial epoxy resins were the reaction products of epichlorohydrin and bisphenol A, the reaction giving the diglycidyl ether of bisphenol A and higher-molecular-weight species. The structure of the resin, ideally, is



The low-molecular-weight liquid products have an  $n$  value about 1 or below. Above  $n = 1$ , the resins are brittle solids.

This chapter outlines the synthesis of these resins. It also describes the use of other hydroxyl-containing molecules to produce different glycidyl ethers. In



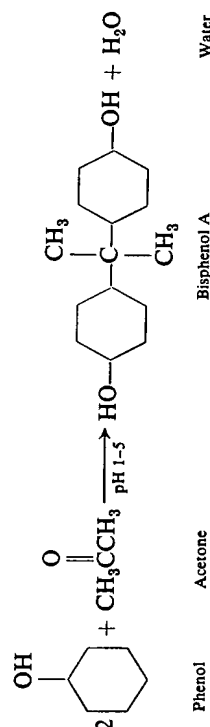
General view of plant for production of epichlorohydrin at Toms River, N.J. (Ciba Products Co.)

addition, the synthesis of glycidyl resins from organic and inorganic acids, from nitrogen-containing compounds, and from silicones, via the epichlorohydrin route is described, as well as the synthesis of other glycidyl resins from monoepoxies by reaction through other functional groups present in the monoepoxy molecule.

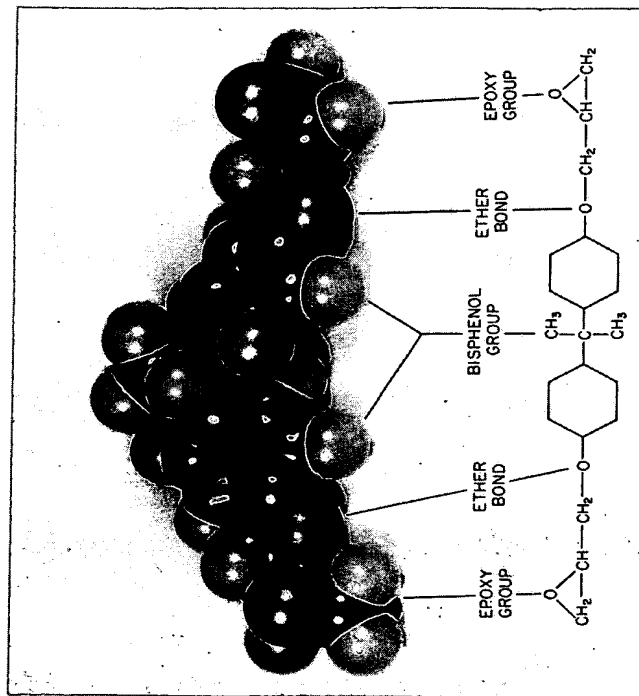
In the synthesis of commercial epoxy resins, epichlorohydrin is the principal epoxidizing reactant. Other epichlorohydrins or dihalohydrins may be used, but are not economically attractive. Methyl and ethyl epichlorohydrin and mixed isomers of more highly substituted epichlorohydrins have been suggested [143], but their use does not appear to provide commercial advantages.

## DIGLYCIDYL ETHER OF BISPHENOL A (DGEBA)

The raw materials for the commercial synthesis of the DGEBA are epichlorohydrin and bisphenol A. Epichlorohydrin is synthesized from propylene and chlorine with dichlorohydrin as an intermediate. Bisphenol A is produced from phenol and acetone as follows:



Because of the ready availability of the raw materials and the ease of manufacture, bisphenol A is the chief dihydric phenol used in epoxy-resin synthesis.

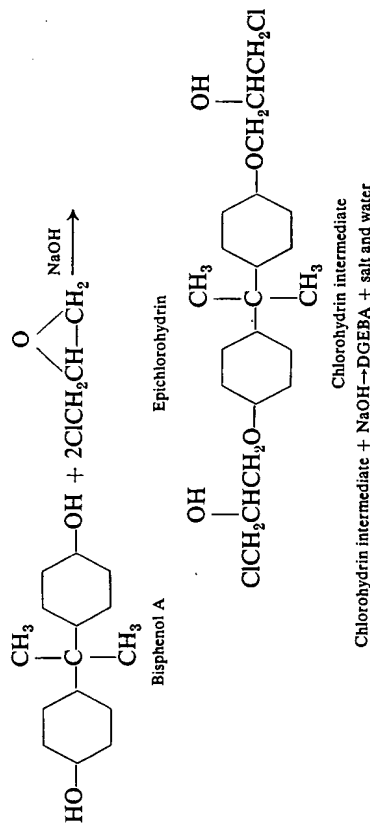


Atom model of the most widely used liquid epoxy resin, diglycidyl ether of bisphenol A (DGEBA,  $n = 0$ ). Approximate magnification: 100 million times. (The Epoxylite Corporation.)

## Synthesis of Monomeric DGEBA

DGEBA is obtained by reacting epichlorohydrin with bisphenol A in the presence of sodium hydroxide [3]. The reaction occurs in two steps: (1) the formation of a chlorohydrin intermediate and (2) the dehydrohalogenation of the intermediate to

the glycidyl ether.



The caustic catalyzes the reaction to produce the chlorohydrin intermediate, acts as the dehydrohalogenating agent, and neutralizes the formed hydrochloric acid.

In order to obtain the monomeric DGEBA, 2 moles of epichlorohydrin is theoretically required for each mole of bisphenol A. However, when this ratio is employed, the monomeric yield is less than 10 per cent, with the remaining material being higher-molecular-weight polymerization products. In order to obtain high yields of the monomeric product, excess epichlorohydrin is employed, the stoichiometric amount being doubled or tripled. Yields of 90 per cent or higher are then possible. Amounts ten times in excess have also been suggested, the "purity" of the diglycidyl ether being dependent on the excess of epichlorohydrin.

#### Synthesis of the DGEBA (mol. wt. ~380)

The DGEBA having an average molecular weight of approximately 380 is the basic liquid epoxy resin in the commercial technology. The synthesis may be conducted as follows:

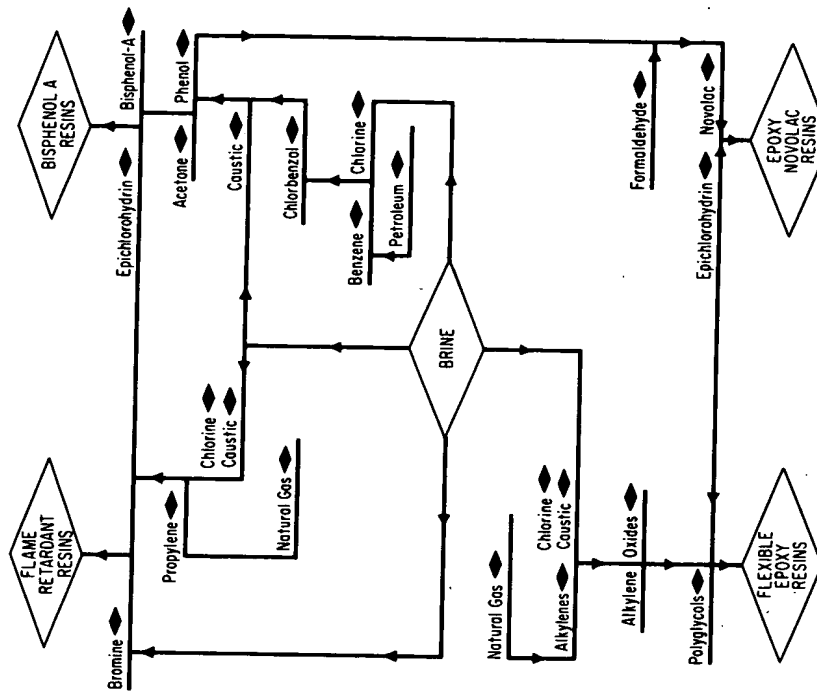
The apparatus employed was a heated reaction vessel with a thermometer, mechanical stirrer, dropping device for admitting aqueous caustic, and a vapor take-off to which was fitted a water-cooled condenser with a thermometer and a condensate collection and separating chamber provided with a return to convey the lower epichlorohydrin layer to the reaction vessel. The separating chamber also had a draw-off and collector for the upper water layer.

The reaction vessel was charged with 1,388 parts (15 moles) of epichlorohydrin and 342 parts (1.5 moles) of bisphenol. The stirrer was started and the solution of bisphenol in epichlorohydrin was heated to 119°C, whereupon the epichlorohydrin began refluxing at a temperature of 112°C. During a period of 3½ hours, 304 parts of 40 per cent aqueous sodium hydroxide (3.0 moles) were added to the boiling reaction mixture. Heating was continued an additional 15 minutes after all the caustic was added. The reaction mixture was then subjected to distillation for removal of unreacted epichlorohydrin.

In order to separate salt from the crude product, approximately 550 parts of toluene was added with stirring and the mixture was filtered, the salt cake being washed with additional toluene and the washing combined with the filtrate. The mixture was then subjected to distillation for removal of toluene, the mixture being heated to a temperature of 170°C at 2 mm pressure. The resulting viscous product, obtained in amount of 509 parts, had a Durrans' Mercury Method softening point of 6°C, had an epoxy value of 0.519 epoxy equivalents per 100 grams, and contained 0.52 per cent chlorine [48].

Various aspects of the synthesis of the lower-molecular-weight species (mol. wt. 380) are covered in the literature. Part of the epichlorohydrin may be reacted, additional added, and the low-molecular-weight epoxy isolated by distilling out the

epichlorohydrin azeotropically [104]. Improved yields are claimed by using caustic in solution with ethanol rather than water [86]. Sodium hydrosulfite may be added to prevent emulsification of resin during the washing operation [89]. An aliphatic secondary alcohol is suggested as an improved solvent to assist in salt removal [59]. Dilute acid is suggested for washing the resin [95]. Chlorine content can be reduced by using only 98 per cent stoichiometric amounts of NaOH

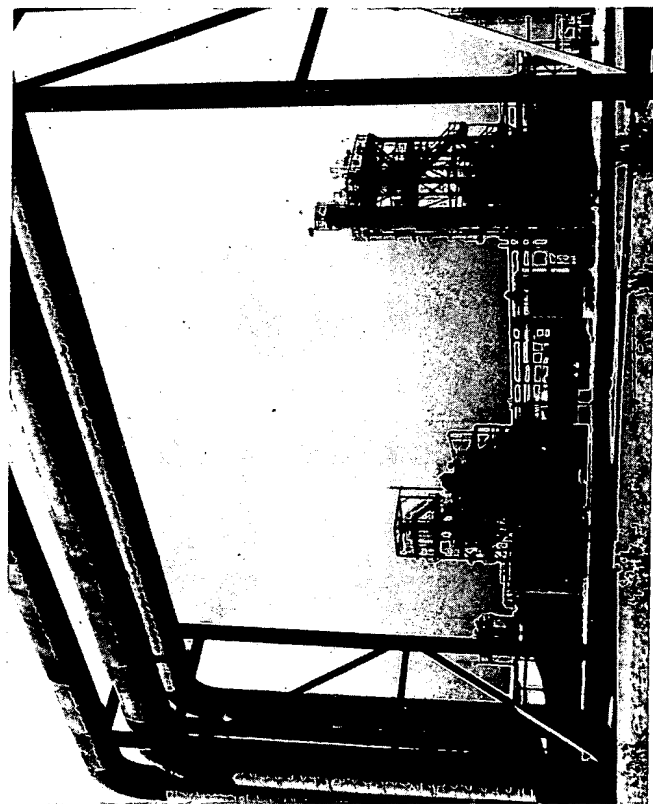


Flow chart showing derivation of commercial epoxy resins via epichlorohydrin route. (Dow Chemical Co.)

and removing excess epichlorohydrin before dehydrohalogenation [63]. Total reflux may be used during the addition of one-half the caustic, with the water formed during the reaction being removed during addition of the last half of the caustic [122]. Monohydric phenols [69] or polypropylene glycol [191] may be added during synthesis in order to reduce viscosity of the resin product. A continuous process for the production of DGEBA (mol. wt. 380) giving a yield of 50 to 80 per cent is described in [63].

An alternative two-step process reacts the bisphenols and epichlorohydrin in an anhydrous medium in the presence of a quaternary ammonium salt [108] or lithium hydroxide monohydrate [99]. The excess epichlorohydrin is then removed before dehydrohalogenation. Interfacial polycondensation techniques have also been used [211].

The intentional production of higher-chlorine-content resins is described in [32]. The anions generated by inorganic bases during the synthesis (see Chap. 5) usually add to the least substituted carbon atom of an unsymmetrical epoxide, but a small but measurable concentration of products arise from reaction at the most substituted carbon atom. These abnormal additions result in production of 1,3-chlorohydrins which are not subject to ring closure. Temperature has been shown to influence the extent to which abnormal addition occurs, being minimized when the initial reaction is accomplished at low temperatures (30 vs. 85°C) and subsequently increased [180]. When ethanol, rather than water, is used with the



Major structures in epoxy-resin plant are framed in arch of pipe at petrochemical complex in Freeport, Tex. (Dow Chemical Co.)

caustic, the primary alcoholic hydroxyls will not react until about 90 per cent of the phenolic hydroxyls have been consumed (i.e., at the point when the alkoxide begins to replace the phenoxide). Reaction of the primary alcohol in preference to reaction of the secondary alcohol along the polymer chain leads to some random chain terminations but eliminates chain branching from the main polymer.

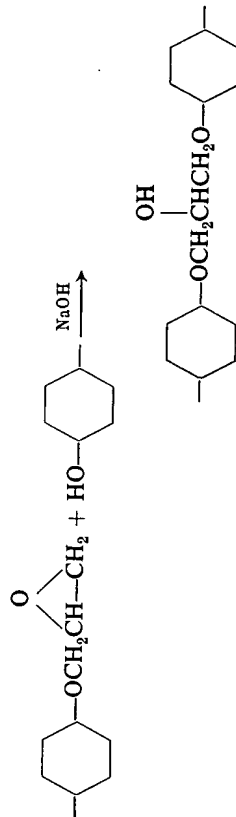
Free-flowing crystals of pure DGEBA are obtained by addition of 10 per cent butyl glycidyl ether to the relatively pure product, cooling to 10°C, and seeding with 0.3 per cent of crystalline DGEBA. After 3 days at low temperature, a 66 per cent yield of pure crystalline material results from treatment of the standard commercial DGEBA resin having a molecular weight of approximately 380 [161].

### Synthesis of Higher-molecular-weight DGEBA

As may be seen from the preceding discussion, it is possible to synthesize higher-molecular-weight epoxy resins by reacting epichlorohydrin and bisphenol A in the presence of excess caustic. The general formula for such a resin has been given

previously. It should be noted that each such molecule contains as many alcoholic hydroxyls as there are repeating units, provided that the molecule is linear with no side branches and contains no more than two epoxy groups.

Synthesis of higher-weight molecules requires not only the consumption of the epoxy groups contained in the epichlorohydrin, but also, in order to link successive bisphenol A groups, the consumption of some of the epoxy groups formed by dehydrohalogenation.



It should, therefore, be possible to govern the degree of polymerization by regulating the ratio of epichlorohydrin/bisphenol A when employing caustic in excess of the amount required to carry out the reaction [26]. Table 2-1 presents

Table 2-1. Effect of Varying Reactant Ratios on Molecular Weight of Epoxy Resins [10]

Mole ratio epichlorohydrin/bisphenol A	Mole ratio NaOH/epichlorohydrin	Softening point, °C	Molecular weight	Epoxide equivalent	Epoxy groups per molecule
2.0	1.1	43	451	314	1.39
1.4	1.3	84	791	592	1.34
1.33	1.3	90	802	730	1.10
1.25	1.3	100	1,133	862	1.32
1.2	1.3	112	1,420	1,176	1.21

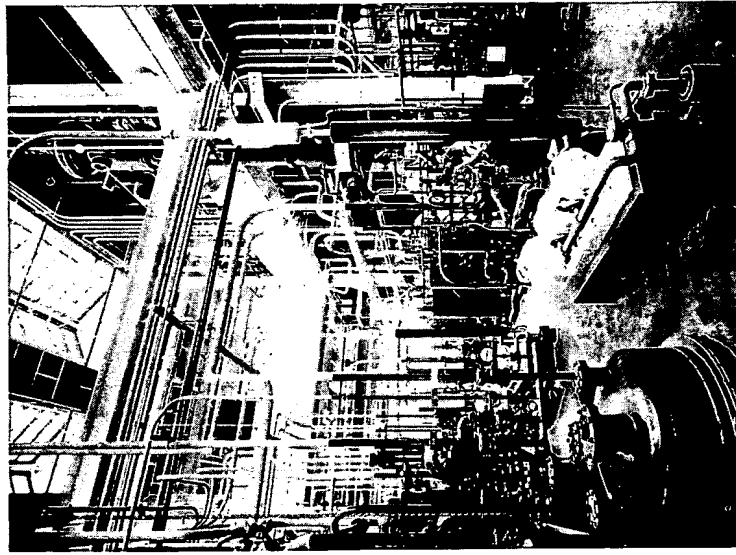
data for various ratios in terms of resultant molecular weight. In actual practice, it is reported that a slight excess of epichlorohydrin (over the apparently stoichiometric ratio for a given molecular weight) is employed [43]. The need for some excess epichlorohydrin is accounted for by the reaction of some per cent of the epichlorohydrin with sodium hydroxide or with aliphatic hydroxyl groups present in impurities to form a variety of by-products, mostly glycerol derivatives. The reaction proceeds in a caustic medium slower than the phenol-epoxy reaction. A study of the kinetics of the overall reaction is given in [136].

A description from the literature illustrates the synthesis of higher-molecular-weight resins, using 1.12 moles epichlorohydrin/1 mole bisphenol A and employing heat and pressure to regulate the reaction.

The apparatus used was a 7½ gallon steam-jacketed pilot-plant kettle, capable of operating under pressure and equipped with a heavy-duty anchor-type agitator, a thermometer, a hot-water inlet, an adjustable level water take-off line, a gas pressure line with gage and pressure regulator, a vapor outlet line and a loading port and a sight glass in the top of the kettle.

The kettle was loaded with a mixture of 14,950 parts of water, 1,483 parts of commercial caustic soda (98.5 per cent NaOH), 17 parts of sodium orthosilicate, and 6,835 parts of bisphenol. After agitation for several minutes at 50°C, 3,000 parts of epichlorohydrin were added to the reaction mixture and the loading port was closed immediately, agitation being continued. With the exothermic heat of reaction and the external heat, the reaction

temperature was brought to 115°C over a period of 30 minutes. Compressed air was introduced and the pressure inside the kettle was adjusted to 25 psi, and held during a 30 minute reaction period at 115°C. The pressure was then increased to 30 to 35 psi to cause the taffylike resinous product to settle to the bottom of the kettle, and as much as possible of the upper water layer was removed with the adjustable-level water take-off line. The taffylike resin was then washed free from the salt and alkali by introducing preheated hot water to the kettle and simultaneously allowing water to flow from the kettle. During the washing period, the resin was continuously agitated. The pressure in the kettle was



General view of supply lines, kettles, and controls for the production of epoxy resins. (Ciba Products Co.)

held at 30 to 35 psi, and the temperature was gradually increased from 120°C to 135°C. After 2½ hours of continuous washing, the water coming from the kettle was neutral. It is important that all of the unreacted alkali, when present, be removed to prevent further polymerization of the resin. After washing was completed, as much water as possible was removed from the kettle through the water take-off line. The air-pressure line was closed and the steam pressure in the jacket increased to raise the temperature of the resin to 137 to 138°C. The steam formed on heating the taffylike resin was slowly released, and, after the pressure had been completely released, the loading port was opened and the last traces of water were removed by heating the resin to 150°C. The resin was continuously agitated during the drying process. The hot resin was then poured from the kettle into a receptacle and allowed to cool [25].

In order to facilitate the washing operation, it has been suggested that an organic solvent, such as high-flash naphtha, be employed during resin synthesis [39]. Removal of the last traces of water may be accomplished by use of a stripping solvent, such as methyl isobutyl ketone [58].

A second process is available for the synthesis of higher-weight resins to eliminate the difficulties involved in washing the contaminants from the compounds melting above 80°C [16,17]. This process requires two steps: (1) the synthesis of a suitable low-molecular-weight resin, say predominantly  $n = 2$ , and (2) the reaction of this material with a calculated charge of bisphenol A in the presence of a trace amount of caustic, which further reacts the terminal epoxy groups with the terminal phenolic hydroxyls of the bisphenol A. The polymerization takes place without the evolution of by-products. In this case the chlorine content should be less than 0.3 per cent for the complete reaction with the charge of bisphenol A [63]. If the labile chlorine content is too high, it will consume the caustic, and if excess caustic is used to overcome this difficulty, erratic polymerization occurs. It has been suggested that lithium hydroxide [127] or lithium salts such as lithium chloride [126] may be employed at about 0.006 per cent (based on the weight of the bisphenol) in place of the caustic, to permit the reaction to be conducted at higher chlorine contents.

A study of the reactions in the synthesis of these higher-molecular-weight species indicates that with low chlorine contents, undesirable side reactions can be suppressed by using a reaction temperature no higher than about 170°C, to give, in the presence of caustic, under optimum conditions, about 93 per cent of the total reaction between the epoxy groups and the phenolic hydroxyls, and to achieve an even distribution of molecular weight [78].

Higher-molecular-weight resins with a narrower molecular-weight-range distribution have been reported when excess bisphenol A is reacted with epichlorohydrin to form a prepolymer and additional epichlorohydrin is subsequently added before dehydrohalogenation [164,210].

A small amount of divalent tin (e.g., stannous chloride [41]) or ferrous sulfate [209] may be added during synthesis to improve color of the higher-molecular-weight resins. Phosphoric acid may be added at the end of the synthesis to increase reactivity with urea or melamine resins [30].

### **Synthesis of Polyhydric Phenol Polyether Alcohols**

It should be possible to create molecules of immense size from epichlorohydrin and bisphenol A. If an equimolar ratio were employed, the molecule formed would theoretically be equal to the combined weight of all the component adducts, with an aromatic hydroxyl at one end of the chain and an epoxy group at the other. In practice, of course, the reaction starts at many reactive points simultaneously, and as the molecular weight increases, the resin mobility decreases and the chain building terminates randomly. Nonetheless, when a 1/1 ratio is employed, very high molecular weight thermoplastic materials are developed [13].

For ester coatings, in which the hydroxyls on the chain are of greater interest than the epoxy groups, it is desirable to regulate the length of this polymeric chain, and monofunctional reactants, such as phenol or ethylene oxide, can be employed in calculated amounts to end-stop polymerization and yield polyhydric phenol polyether alcohols of almost any given molecular weight [9]. These higher-weight molecules [37] will contain a number of alcoholic hydroxyls, advantageously 20 or more [4], capable of direct esterification. Under suitable reaction conditions (i.e., ester interchange) epoxy groups may be preserved during the esterification operation [23].

A two-step process for the manufacture of the higher-molecular-weight species has been developed which involves addition of a calculated charge of bisphenol A, together with a calculated charge of a monofunctional drying acid, to the low-molecular-weight resin [113]. A base catalyst is used to ensure, first, the acid-epoxy reaction to regulate the molecular weight, and, second, the phenol-epoxy reaction

to obtain the desired chain length. After completion of the epoxy-phenol reaction, the remaining drying acid can be added to the same vessel and reacted by conventional esterification procedures to produce the varnish.

As used in ester coatings, polyhydroxy polyethers derived from epichlorohydrin and bisphenol A, although containing few if any epoxy groups, are by custom referred to in the industry as *epoxy resins*, since they are synthesized from the basic reactants for diglycidyl ethers.

The very high molecular weight (e.g., mol. wt. 30,000 and higher) thermoplastic resins are designated *phenoxy resins* and are employed as coatings, adhesives, and molding compounds.

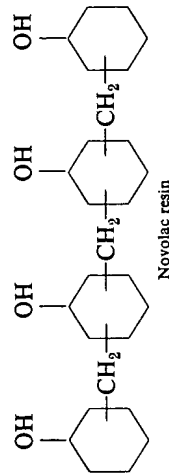
Properties of the phenoxy resins are varied by varying the molecular weight of the polymer. Additionally, variations may be obtained by using more than one type of bisphenol to obtain thermoplastic random and alternating copolymers [174]. Like the lower-molecular-weight species, the phenoxy resins may also be esterified to produce coatings resins [173].

The phenoxy resins based on epichlorohydrin and bisphenol A appear to be unbranched and highly linear below a molecular weight of about 70,000. Above that weight they are abruptly and increasingly branched to a very high degree [166].

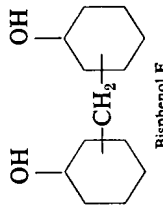
Aside from a brief discussion on their use in coating formulations in Chap. 24, the polyhydric phenol polyether alcohols are not otherwise considered in this book.

### GLYCIDYL ETHERS OF NOVOLAC RESINS

Novolac resins [70] are produced by the reaction of phenol and formaldehyde in acid solution. Such resins have the following idealized structure:



The simplest novolac could be considered to be bisphenol F with the novolacs

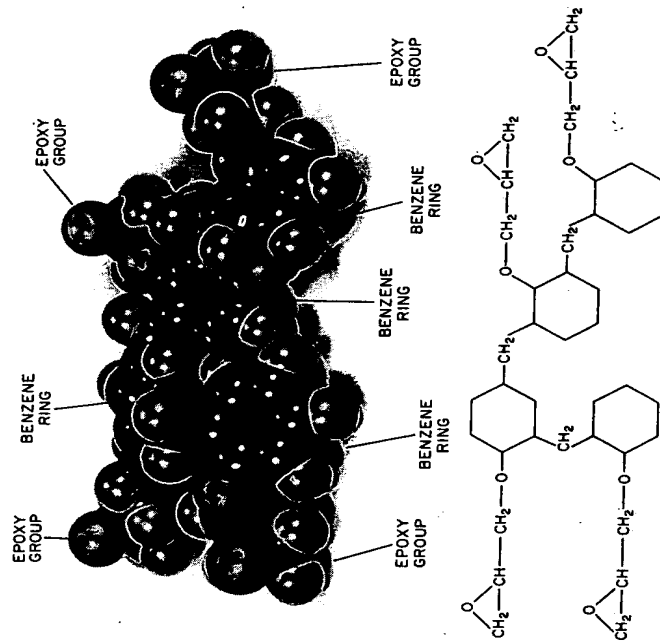


ranging upward in molecular weight from this to compounds containing 10 to 12 phenolic hydroxyls. Such resins are suitable intermediates for the synthesis of polyglycidyl ether resins.

The novolac-based epoxy resins are synthesized by reaction with epichlorohydrin in the same fashion as are the bisphenol A resins. The number of glycidyl groups per molecule in the resin is dependent upon the number of phenolic hydroxyls in the starting novolac, the extent to which they are reacted, and the extent to which the lowest-molecular-weight species are polymerized during synthesis. Theoretically all the phenolic hydroxyls may be reacted, but in practice selective epoxidation offers an advantage when the novolac contains more than three phenolic hydroxyls. Should complete epoxidation be accomplished, steric factors will prevent the reaction of some of the epoxy groups during cure [77].

Synthesis of a low-molecular-weight novolac, as a starting point for the production of an epoxy resin, may be conducted as follows:

94 parts of U.S.P. phenol (1 mole) and 94 of water were charged into a reactor. 2.9 parts of concentrated sulfuric acid (96.6 per cent) were added, to give a pH of 0.5. The acidified solution was heated to 80°C. Then 34.1 parts of 44 per cent aqueous solution of formaldehyde (0.5 mole) were added to the stirred acidified solution, over a period of 4 hours, while the temperature was maintained at 80°C.



Atom model of epoxylated phenol-formaldehyde novolac resin showing massive, oxidation-resistant aromatic structure. Magnification approximately 100 million times. (*The Epoxylite Corporation.*)

Upon completion of the formaldehyde addition, the temperature was maintained at 80°C for an additional period of a half hour, after which 4 parts of sodium carbonate were added to neutralize the acid. The system was then placed under vacuum at a pressure of 30 mm mercury and water distilled therefrom by heating until the temperature reached 80°C. At this point, additional water was then added slowly to the system at a rate such that the distillation temperature was maintained at approximately 80°C. The water addition and distillation was continued until the total distillate collected amounted to 315 parts [62].

The resultant novolac resin is a solid at room temperature.

In addition to phenol, alkyl-substituted phenols such as *o*-cresol may be used as a starting point for the production of novolac. If at least four carbon atoms are present in the alkyl group, these novolacs can be epoxidized to yield resins soluble in paraffin hydrocarbons [31]. The novolac may be based on chlorinated phenols to impart flame resistance to the cured compositions [19].



The novolac resins may be partially esterified before the epoxidation reaction [75] or esterified afterward for use in ester coatings [24].

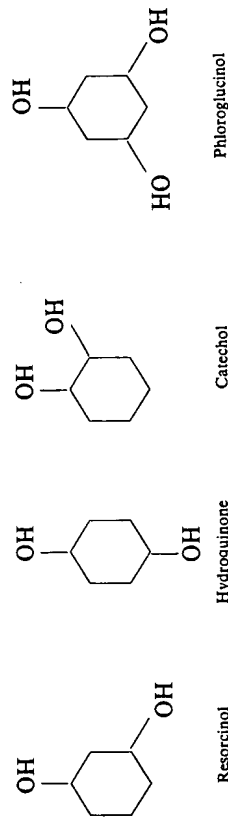
The glycidyl ethers of novolacs are of increasing commercial importance because of their higher functionality.

## GLYCIDYL ETHERS OF OTHER AROMATIC COMPOUNDS

For convenience, we can divide the remaining aromatic-based glycidyl ether epoxy resins into three classes: those based on mononuclear phenols, those based on binuclear phenols, and those based on polynuclear phenols. These resins are synthesized, as before, by reaction with epichlorohydrin in a caustic medium.

### Glycidyl Ethers of Mononuclear Di- and Trihydric Phenols

Representative of mononuclear di- and trihydric phenols and substituted phenols are:



The synthesis of the diglycidyl ether of resorcinol has been reported in detail [49,85]. The epoxidation of chlorinated hydroquinones has been described [22]. Substituted hydroquinones which are sterically hindered are epoxidized through the disodium salts [34].

Difficulties have been reported in the synthesis of the triepoxy from phloroglucinol. If the enol form is assumed and sufficient epichlorohydrin is employed to react with all three phenolic hydroxyls, only a diepoxo resin results, and the remaining phenolic hydroxyl reacts with the newly formed resin to produce a polymerized material during dehydrohalogenation. It is possible that changed reaction conditions might overcome the difficulties [134].

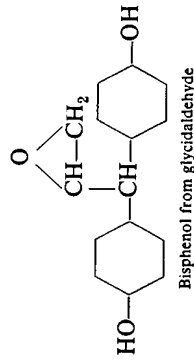
A description of the two-step epoxidation of saligenin, containing both an aliphatic and an aromatic hydroxyl, is given in [142], and epoxidation of vanillyl alcohol is described in [171].

### Glycidyl Ethers of Bisphenols

Dihydric diphenols with a single carbon between the rings are most popular commercially, insofar as they are available from any aldehyde and many ketones and from any phenol having an open ortho or para position. Alternatives to bisphenol A were explored early in the technology, and resins from, for example, 4,4'-dihydroxybenzophenone were reported as early as 1942 [1]. Eighty-four representative bisphenols are given in [57].

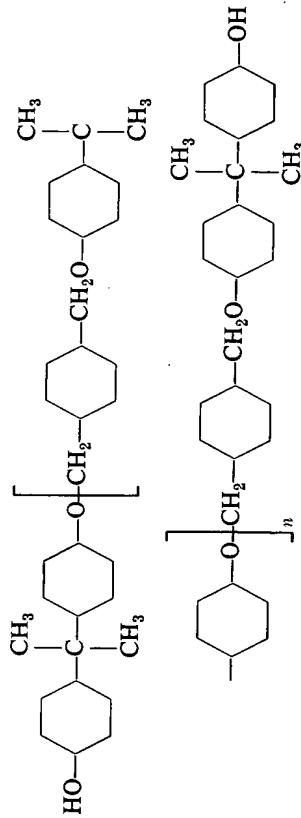
With the bisphenols containing a single carbon bridge, a variety of substitutions on the benzhydryl carbon are possible; epoxidation of unsymmetrical compounds is described in [177]; the effect on epoxidation of chlorine substituents are reported [155,156], and the epoxidation of rosolic acid has been described [176]. With epoxidized aldehydes, an epoxy group may be attached to the benzhydryl carbon,

as for example, when glycidaldehyde is used [120]:



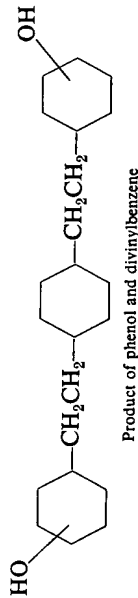
Bisphenol from glycidaldehyde

Bisphenols with more than one carbon atom between rings, although not as common, may be synthesized. The synthesis and epoxidation of a bisphenol from unsaturated polymers of butadiene and phenol is described in [135]. Long, aromatic-containing chains may be introduced by reacting *p*-xylene dichloride and bisphenol A [115], and may be obtained from substituted chlorinated xylenes [116].



Product of *p*-xylene dichloride and bisphenol A

Phenol may be reacted with divinylbenzene to produce a three-ring structure, and hydroxyl-terminated polycarbonates have been epoxidized [160].



Product of phenol and divinylbenzene

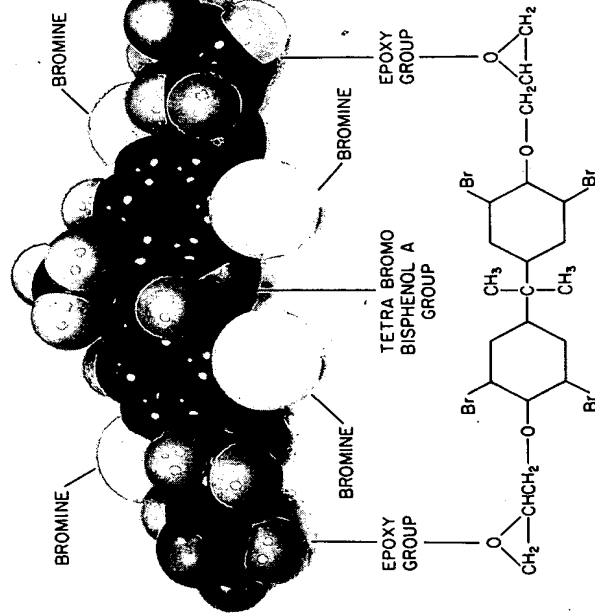
Alternatively, the phenols may be directly connected, as is the case with bisphenol (4,4'-dihydroxybiphenyl) and resorcinol still residues which when epoxidized give 2,3',4'-tri(epoxypropoxy)diphenyl [194]. Or dihydroxynaphthalene may be used [83], as may dihydroxyfluoranthene [101], dihydroxydinaphthylmethane [154,165,207], and the yellow form of fluorescein [168].

The bisphenols may contain alkyl or aryl substituents [20,81], and the substituents may contain hydroxyl groups [29,205]. Hydroxyl-containing bisphenols such as 3,3-bis(4-hydroxyphenyl)-1,2-dihydroxypropane [82] may be used, as may mixed phenols from coal tars [72,157]. Phenol may be condensed with 3,9-divinylspirobi(*m*-dioxane) to give a diphenol containing a cycloaliphatic backbone that is similar to that of the cycloaliphatics from pentaerythritol described in Chap. 3 [188].

Of the substituents, perhaps the most interesting are the halogenated bisphenols. Both tetrabromo- and tetrachlorobisphenol A have been investigated. The synthesis of the tetrachloro species has been reported in detail [71,73], although the tetrabromo compound has proved superior and considerable work has been devoted to its synthesis. The diglycidyl ether of tetrabromobisphenol A may be crystallized from cyclohexane at purities of better than 99 per cent [199]. It has

been reported that bromine may be added during synthesis of DGEBA to produce a brominated species whose flame resistance is further enhanced by the addition of antimony *sec*-butoxide at 110°C to the final resin [196]. Tetrachloro and bromo versions of the bisphenol from phenol and hexafluoroacetone have been epoxidized [213].

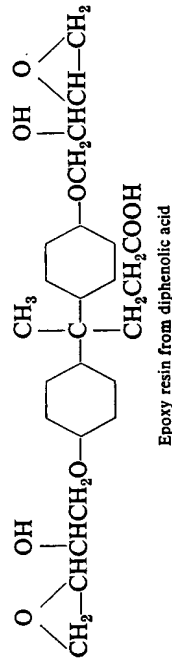
Suitable bisphenols, then, may range from the simplest structures, such as condensation products of phenol with acetylene [130], 2-butanone, and acetone with *o*-cresol; through materials of increased functionality, such as 2,4,4'-trihydroxydiphenyldimethylmethane; to compounds with fairly complex side chains, such as



Atom model of diglycidyl ether of tetrabromobisphenol A. The marked change in physical properties often encountered when using chlorinated and brominated resins is clarified by examination of the significantly larger size of the chlorine or bromine atoms compared to the carbon, hydrogen, and oxygen atoms. Approximately 100 million times actual size. (*The Epoxylite Corporation.*)

1,8-bis(4-hydroxyphenyl)pentadecane from cashew nutshell liquid and phenol [183] or the similar compound based on substituted catechol (Bhilawanol) and phenol [192], and diphenols condensed with dihaloalkyl ethers (e.g., 2,2'-dichlorodithyl ether) [118]; to compounds containing other atoms, such as, for example, sulfur in place of the benzydryl carbon as with dihydroxydiphenylsulfone [33]. A review of sulfur-containing epoxy resins is contained in [131].

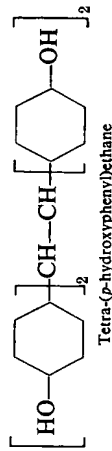
Carboxyl-containing epoxy resins, such as the epoxy resin from diphenolic acid,



have been synthesized in a three-step process [93,100]. In the first step, the carboxyl group is converted to the carboxylate salt (COONa). In the second step, a diepoxyl, such as butadiene dioxide is reacted with the phenolic hydroxyls in a strong solvent to prevent loss of epoxies. The carboxylate salt is then converted back to the carboxyl group by treatment with a strong acid. It is interesting to note that use of the diepoxyl rather than the epichlorohydrin results in the production of additional hydroxyl groups, as indicated in the structure. In addition, the reaction when the diepoxyl is employed, does not involve the evolution of by-products, and chlorine, even in trace amounts, will be absent from the final product since none need be introduced during synthesis. Diphenolic acid has been reacted with epichlorohydrin to produce a triepoxy resin, the third epoxy group being a glycidyl ester.

### Glycidyl Ethers of Polynuclear Phenols

Tri- and tetranuclear phenols have been employed as coreactants with epichlorohydrin for the production of glycidyl ethers [52,56]. The synthesis of the tetraglycidyl ether from tetra(*p*-hydroxyphenyl)ethane is described in [65].



The synthesis of tri- and tetraglycidyl ethers from the reaction product of phenol and acrolein is described in [46]. The triphenol from phosphoric acid and bisphenol A has been epoxidized [178]. Epoxidized polyphenols have been synthesized from phenols and chloroacetones [111], from phenols and polycarbonyl-substituted benzenes [175], from phenols and vanillyl alcohol [170], from phenol-xylene-formaldehyde [162], and from formaldehyde and 2,7-dihydroxynaphthalene [172]. The synthesis of polyglycidyl ethers from the reaction product of resorcinol and acetone is described in [112].

Many of these polyphenols are closely related to the novolac resins as previously discussed, in the main being derived from the condensation products of phenols and polyphenols with aldehydes, ketones, etc.

A variety of complex polyphenols, substantially different from aldehyde-phenol reaction products, may be developed from diphenolic acid.

Two moles of diphenolic acid may be reacted through the carboxyl groups with suitable difunctional molecules to produce tetraphenols of the following generalized structure:

